Estimation of Closed Cup Flash Points of Combustible Solvent Blends

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A simple formulation is developed for the accurate estimation of flash points of miscible combustible solvent mixtures. It consists of an equation, which was previously validated for pure compounds. It is shown that this procedure allows accurate estimations for ideal and nonideal binary and ternary mixtures. This method does not need prerequisites such as the lower flammability limits of pure components and the use of the Le Chatelier law. © *2006 American Institute of Physics.* [DOI: 10.1063/1.1928236]

Key words: flammability data; flash points; hazards; ignition; safety.

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1. Introduction

We recently proposed an empirical equation for the accurate estimation of flash points (FPs) (in air at atmospheric pressure) of pure compounds:

$$\mathrm{FP}(K) = 1.477 \times T_{\mathrm{eb}}^{+0.79686} \times \Delta_{\mathrm{vap}}H^{\circ\,+0.16845} \times n^{-0.05948}$$

where T_{eb} is the normal boiling point of the compound expressed in K, $\Delta_{\mathrm{vap}}H^{\circ}$ the standard enthalpy of vaporization at 298.15 K of the compound expressed in kJ mol^{-1}, and n the number of carbon atoms in the fuel molecule.[1] This equation was validated with data from approximately 600 compounds.

The reliable estimation of flash point of a mixture is also of interest since liquid fuel mixtures are often used in industrial processes. As underlined by Gupta and Olson,[2] such a method will allow the development of solvent blends and other chemical products having desired flash point values to

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meet standards. The prediction of safety related properties can also reduce the time and amount of work needed to develop new products. Several methods have been proposed in the past for estimation of the flash points of mixtures.[3–6] A review of some of the methods has been recently published by Vidal *et al.*[7] The most reliable of these methods[5,6] are used together with the Dalton law, the Raoult law for ideal solutions, the corrected Raoult law for nonideal solutions, the Clausius–Clapeyron equation (or the Antoine equation), and the Le Chatelier law. In all these methods, the flash point is calculated iteratively. Although quite accurate for many of the gaseous fuel mixtures (more exactly here gases are vapors), the Le Chatelier law, which allows the calculation of the lower flammability limit (LFL) of a fuel mixture from the knowledge of the LFL of each compound, has some limitations and an incorrect evaluation of the LFL of a gas mixture at a given temperature above a liquid at the same temperature should lead to an incorrect flash point temperature estimation. Moreover, LFLs are not known for all the compounds and this hampers the use of the Le Chatelier law and the estimation of the flash point of the fuel mixture. The temperature dependence of LFLs is also not known for many of the compounds and, although the temperature dependence is quite weak in the 25–100 °C range, LFLs at flash point temperature are needed to use the Le Chatelier law following this procedure. Furthermore, the iterative procedure needed for determination of the flash point of a fuel mixture is quite tedious; in particular for nonideal solutions for which the calculations of activity coefficients are requested.

In this study we examine the validity of the equation established for pure compounds to predict the flash points of mixtures of fuels. It was shown that this equation allows an accurate estimation of flash points for about all the chemical families and also for polyfunctional compounds.[1] It was also shown that this equation is able to predict correct flash points for isomers. To assess the validity of this equation for fuel mixtures, extensive validation is needed. However, flash point data of fuel mixtures are quite scarce in the literature[3–6] and the present study will rely on the literature data. Additional experimental studies are in process to help further support this work. These results will be presented elsewhere.[8]

2. Flash Point Estimation Procedure

Data needed for the use of the equation, as presented in Sec. 1 are as follows:

(1) normal boiling point T_{eb} of the fuel mixture will be discussed in Sec. 3;
(2) standard enthalpy of vaporization, $\Delta_{vap}H°(298.15\ \mathrm{K})$ of the fuel mixture as expressed in $\mathrm{kJ\,mol^{-1}}$ will be discussed in Sec. 4; and
(3) n, the average number of carbon atoms in the fuel mixture, will be discussed in Sec. 5.

In dealing with a fuel mixture, the composition of the gas phase must be known. There are several publications which deal with vapor–liquid equilibrium (VLE) experimental data. These should be consulted first. However, a powerful option for all mixtures, ideal or nonideal, are those techniques for which activity coefficients have been estimated. UNIFAC[9–14] is a group contribution based model for estimation of liquid phase activity coefficients γ_i of nonelectrolytic mixtures. The group-interaction parameters needed are calculated using 14 000 VLE data and these groups allow the prediction of VLE at low to moderate pressures in the 250–425 K temperature range. It is beyond the scope of this paper to describe in detail the UNIFAC method, which is described in several papers.[9–14] Attempts have been made to improve the predictions of the UNIFAC method by other groups[15,16] and although several other methods (Margules equations, van Laar equation, and NRTL method, among others)[17] exist, the UNIFAC method is the most widely validated, used, and probably the most predictive. The main advantage of UNIFAC is its wide range of application and the main drawback is that the UNIFAC method is mathematically uneasy to handle and the calculations are therefore tedious. To overcome this difficulty, the VLE calculator of Kovats,[18] called VLECalc, has been used to calculate the activity coefficients γ_i. These γ_i coefficients are needed for calculating the normal boiling point of the liquid mixture for which a flash point temperature calculation is requested and also for the standard enthalpy of vaporization at 298 K of this liquid mixture.

3. Determination of the Normal Boiling Point of the Fuel Mixture

The normal boiling point T_{eb} is determined according to $\Sigma_i P_i = 760$ Torr with P_i the partial pressure of compound i in the gas phase above the liquid at $T = T_{eb}$. Partial pressures P_i are calculated according to $P_i = x_i \gamma_i P_{isat}$ where x_i is the mole fraction of compound i in the liquid phase ($\Sigma_i x_i = 1$), γ_i the activity coefficient of compound i in the liquid fuel mixture at T_{eb}, and P_{isat} is the vapor pressure of pure compound i at T_{eb}. P_{isat} as a function of T is available in several compilations for many of the compounds either tabulated[19,20] or expressed according to the Antoine equation.[17,19,20,21] Normal boiling points can be estimated with the calculator of Kovats.[18]

4. Determination of the Standard Enthalpy of Vaporization at 298.15 K

The standard enthalpy of vaporization at 298.15 K is calculated according to the Clapeyron equation applied to liquid–vapor equilibrium, also called the Clausius–Clapeyron law, from the slope of $\ln P = f(1/T)$, with T in Kelvin, which is equal to $-\Delta H^{\circ}_{vap}/R$ where $P = \Sigma_i P_i$ at T, where $P_i = x_i \gamma_i P_{isat}$, and P_{isat} is the vapor pressure of pure compound i at T, and γ_i the activity coefficient of compound i at T and x_i is the mole fraction of compound i in the liquid phase. Three temperatures in the vicinity of 298.15 K (25 °C) have been considered for this linear $\ln P = f(1/T)$

TABLE 1. Normal boiling point, vapor pressures at 20, 30, and 35 °C, and resulting enthalpy of vaporization at 298.15 K (assumed to be constant in the 20–35 °C temperature range) for some n-octane/n-heptane mixtures. $\Sigma_i x_i = 1$, $x_{\text{n-octane}}$ is the mole fraction of n-octane in the binary liquid mixture n-octane/n-heptane.

$x_{\text{n-octane}}$	Normal boiling point T_{eb} (°C)	Vapor pressure 20 °C (Torr)	Vapor pressure 30 °C (Torr)	Vapor pressure 35 °C (Torr)	Enthalpy of vaporization $\Delta_{\text{vap}}H°(298\text{ K})$ (kJ mol^{-1})
0.1	100.25	33.02	54.5	68.98	36.87
0.2	102.35	30.50	50.48	63.97	37.07
0.4	106.98	25.48	42.44	53.96	37.55
0.6	112.26	20.45	34.42	43.97	38.31
0.8	118.36	15.45	26.42	34	39.47

regression, namely, 20, 30, and 35 °C. The three vapor pressures can also be estimated with the calculator of Kovats.[18]

5. Determination of *n*

For pure compounds, in the equation n represents the number of carbon atoms in the compound. Here n represents the number of carbon atoms in a fictitious compound representative of the fuel vapor mixture above the fuel liquid mixture. It is defined as $n = \Sigma_i y_i n_i$, where n_i is the number of carbon atoms in the compound i and y_i is the mole fraction of compound i in the fuel vapor mixture above the liquid at the flash point temperature. However, because the flash point (FP) temperature is unknown, y_i is defined here as the mole fraction of compound i in the fuel vapor mixture above the liquid at the normal boiling point (BP). Although the compositions of the vapor phase at both temperatures are different since the activity coefficients are temperature dependent, this assumption holds because

$$\left(\frac{n_{\text{FP}}}{n_{\text{BP}}}\right)^{-0.05948} \approx 1,$$

where n_{FP} is n, as defined above, at the flash point temperature of the mixture under consideration and n_{BP} is n, as defined above, at the normal boiling point of the mixture under consideration. When necessary (however it is exceptionally the case), i.e., if the composition of the vapor at the flash point is expected or shown to be very different from the composition of the vapor at the normal boiling point, it can be proceeded iteratively. Mole fractions in the fuel vapor mixture y_i can be estimated readily with the calculator of Kovats, whatever the temperature of the liquid solution is.[18]

6. Determination of the Flash Point Temperature

Once all the data needed are known, the flash point temperature is determined by using the equation

$$\text{FP}(K) = 1.477 \times T_{\text{eb}}^{+0.79686} \times \Delta H_{\text{vap}}^{\circ\,+0.16845} \times n^{-0.05948},$$

which is exactly the same equation as the one established for the pure compounds.[1] The two advantages of this equation are: that LFL data are not required for the calculation of the flash point of the solution and the same equation is used for pure substances as well as mixtures.

7. Results and Discussion: Validation of the Equation

Data available in the literature concerning the flash points of fuel mixtures are quite scarce.[22] Fuel mixtures can be divided into two categories: ideal solutions and nonideal solutions. Ideal solutions are solutions for which the activity coefficients γ_i are equal to 1 for all compounds: these solutions follow the Raoult law. Nonideal solutions are solutions for which the activity coefficient γ_i is not equal to 1 for at least one compound in the solution. All the solutions studied here, ideal and nonideal, are treated following the same procedure, which is discussed in Sec. 2.

7.1. Binary Mixtures

7.1.1. n-Octane/n-Heptane Mixtures

The UNIFAC method predicts that the activity coefficients are about equal to one for both compounds in wide temperature and composition ranges, i.e., these compounds form, as expected, an ideal solution. Table 1 gives the normal boiling point, the vapor pressures at 20, 30, and 35 °C and the resulting enthalpy of vaporization computed for n-octane/n-heptane mixtures, which are the data needed to use the equation, and Fig. 1 compares the experimental flash points and the calculated ones with the equation. The agreement between calculations and experiments is excellent. Mean absolute deviation is 1.4 °C and maximum absolute deviation is 2 °C. Tables such as Table 1 have been established for all the following mixtures but are not reported in this paper. Only figures are then reported.

7.1.2. n-Decane/n-Dodecane

The n-decane/n-dodecane solutions are also ideal solutions. Figure 2 compares the experimental flash points and the calculated ones with the equation. The agreement between calculations and experiments is correct. Mean absolute deviation is 4 °C and maximum absolute deviation is 4.7 °C.

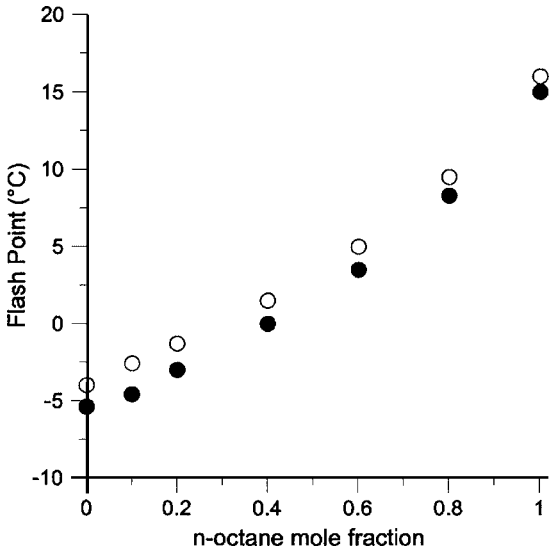

FIG. 1. Comparison between calculated and experimental flash points for n-octane/n-heptane mixtures.

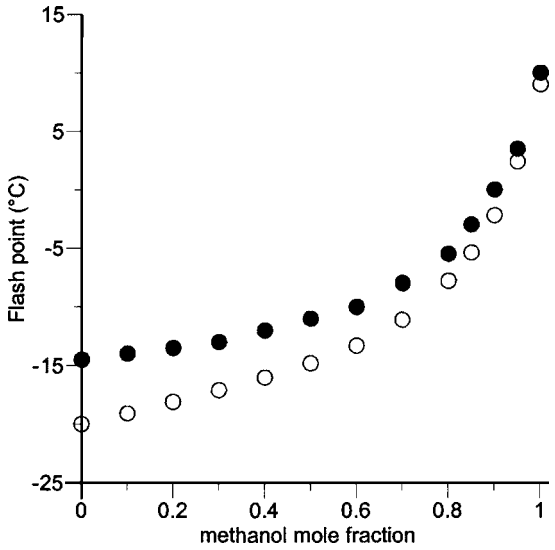

FIG. 3. Comparison between calculated and experimental flash points for methanol/methyl acetate mixtures.

7.1.3. Methanol/Methyl Acetate

These compounds do not constitute ideal solutions. Activity coefficients in the range between approximately 1 and 3, depending on the composition, have been computed by using the UNIFAC method. Figure 3 compares the experimental flash points and the calculated ones with the equation. The agreement between experiments and calculations is good: mean absolute deviation is 2.6 °C and maximum absolute deviation is 6 °C.

7.1.4. n-Octane/Ethanol

n-octane/ethanol solutions are highly nonideal solutions. These mixtures are particularly interesting because they exhibit flash point temperatures below the flash points of both the pure compounds. For safety reasons, these features need to be correctly predicted and the assumption quite commonly expressed that the flash point of a solution cannot be lower than the lowest flash point of the pure compounds constituting the solution is clearly wrong. Figure 4 compares the experimental flash points and the calculated ones with the equation. The agreement between experiments and calculations is good: mean absolute deviation is 2.3 °C and maximum absolute deviation is 4.5 °C.

7.1.5. n-Octane/1-Butanol

As expected, these compounds also constitute highly nonideal solutions. Activity coefficients with values between about 1 and 6 have been computed by using the UNIFAC

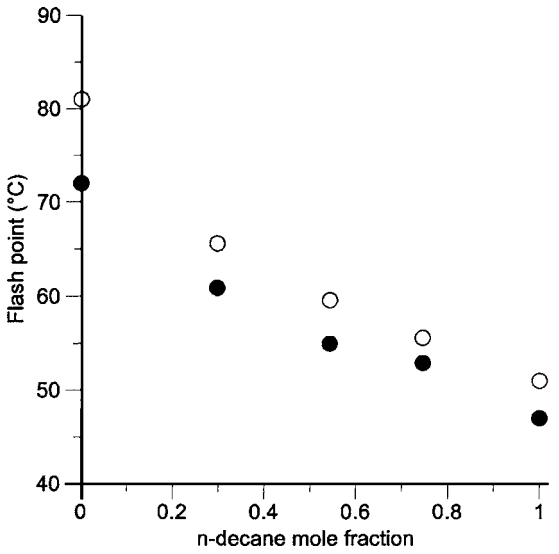

FIG. 2. Comparison between calculated and experimental flash points for n-decane/n-dodecane mixtures.

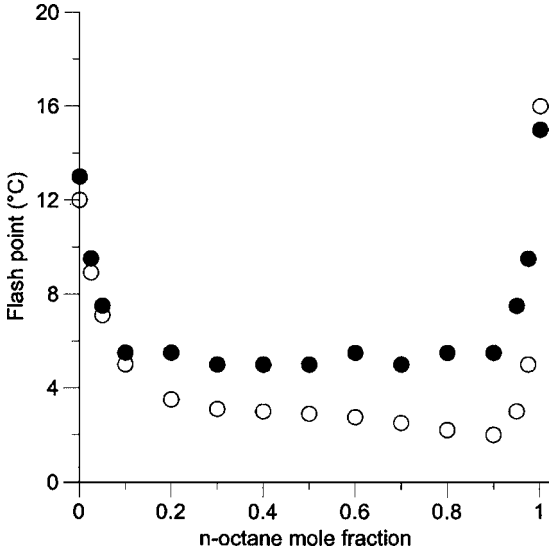

FIG. 4. Comparison between calculated and experimental flash points for n-octane/ethanol mixtures.

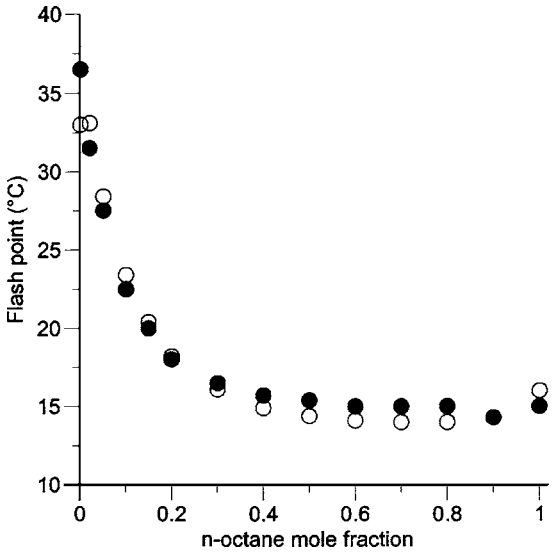

FIG. 5. Comparison between calculated and experimental flash points for n-octane/1-butanol mixtures.

method. Figure 5 compares the experimental flash points and the calculated ones with the equation. The agreement is found to be good. Mean absolute deviation is 0.8 °C and maximum absolute deviation is 1.6 °C.

7.1.6. Isobutanol/Toluene

As expected, these compounds also constitute highly nonideal solutions. Figure 6 compares the experimental flash points and the calculated ones with the equation. The agreement is found to be good. Mean absolute deviation is 1.4 °C and maximum absolute deviation is 3.7 °C.

7.1.7. Methanol/Acetone

Figure 7 compares the experimental flash points and the calculated ones with the equation. The agreement is found to be good.

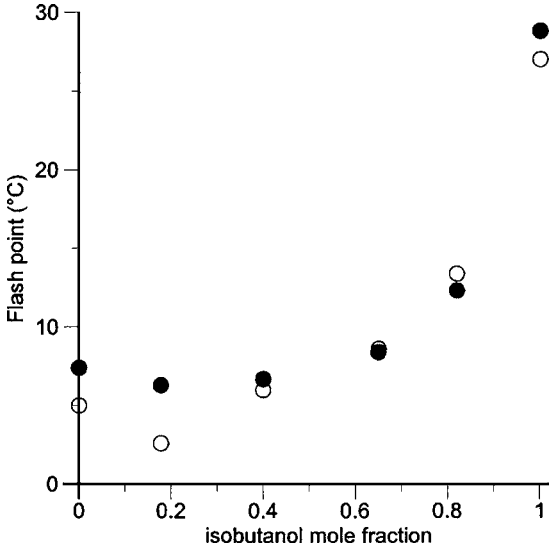

FIG. 6. Comparison between calculated and experimental flash points for isobutanol/toluene mixtures.

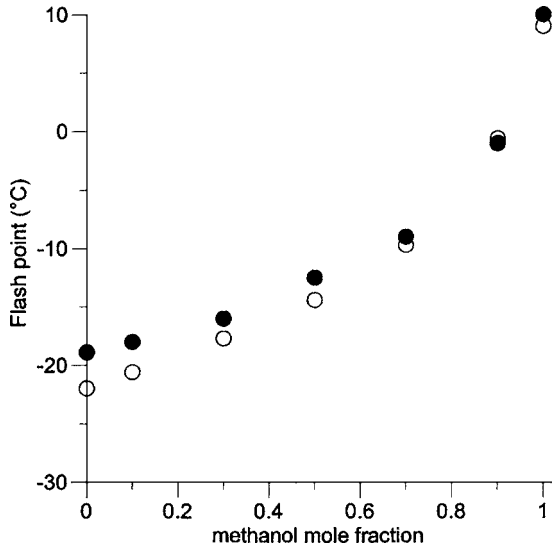

FIG. 7. Comparison between calculated and experimental flash points for methanol/acetone mixtures.

TABLE 2. Ternary mixtures—ethanol/toluene/ethylacetate. Mean absolute deviation is 0.9 °C and maximum absolute deviation is 2.1 °C. Experimental data are from Gmehling and Rasmussen.[3]

$x_{ethanol}$	$x_{toluene}$	$x_{ethylacetate}$	FP (°C) experimental[a]	FP calc (°C) calculated
0.328	0.328	0.344	−3.33	−4.2
0.568	0.284	0.148	−1.67	−1.8
0.564	0.141	0.295	−3.33	−3.8
0.494	0.247	0.259	−2.78	−3.4
0.887	0.055	0.058	2.22	3.1
0.176	0.088	0.736	−5.56	−7.6
0.856	0.114	0.03	1.67	2.8

TABLE 3. Ternary mixtures—methanol/ethanol/acetone. Mean absolute deviation is 1.6 °C and maximum absolute deviation is 3 °C. Experimental data are from Liaw *et al.*[6]

$x_{methanol}$	$x_{ethanol}$	$x_{acetone}$	FP (°C) experimental[a]	FP (°C) calculated
0.1	0.8	0.1	1.3	−1.5
0.8	0.1	0.1	0	−0.7
0.7	0.1	0.2	−5.6	−6.1
0.1	0.7	0.2	−4.3	−7.3
0.6	0.1	0.3	−8.7	−9.7
0.3	0.1	0.6	−14.8	−16.2

7.2. Ternary Mixtures

Very few data are available in the literature. Calculated data with the method proposed here are compared with the experimental data given in Tables 2 and 3. The agreement is found to be very good.

8. Conclusions

A new method is proposed for estimation of the flash point of fuel mixtures. This method consists of an equation primarily established for calculation of the flash points of pure organic compounds. The method proposed is shown to predict accurately the flash points of several binary or ternary mixtures including some very highly nonideal mixtures. The very interesting experimental feature that, for some binary mixtures, the flash point of the solution can be lower than both the flash points of the two pure components of the solution is also correctly predicted. The method proposed here, in contrast with the currently available method, does not require the knowledge of the LFLs of the pure components, the temperature dependence of those LFLs, and the use of the Le Chatelier law. The use of the vapor–liquid equilibrium calculator together with the equation allows a very easy estimation of the flash point of solvent mixtures made with up to six combustible components.

9. Acknowledgments

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